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USE OF TITANIUM DIOXIDE FOR THE DEVELOPMENT OF ANTIBACTERIAL GLASS ENAMEL COATINGS

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It is shown that titanium dioxide is useful for developing antibacterial glass enamel coatings. Antibacterial powder (filler) was synthesized on the basis of hydroxyapatite modified with titanium oxide, and its phase composition was investigated. It was established that the composite glass enamel coatings studied are characterized by a substantial antibacterial and antifungal effect from 70 to 90% with synthesized inorganic filler content from 1 to 5% with $Ti^{4+}/(Ti^{4+} + Ca^{2+})$ ratio equal ratio 0.04 – 0.07.

Key words: glass enamel coating, titanium dioxide, antibacterial properties.

The effectiveness of titanium dioxide for obtaining cover glass enamels for dishware, sanitary-technical articles, and architectural-building articles is widely known. This is explained by the fact that titanium enamels distinguished by good opacification and high mechanical indicators, chemical properties, and aesthetic-decorative characteristics [1].

Today, photocatalytic reactions are being intensively developed using TiO_2. Initially, attempts were made to use the photocatalytic power of titanium dioxide to obtain hydrogen from water; then, the capability of a TiO_2 coating to kill viruses and cancer cells and to decompose organic pollutants attracted rapt attention. At present many companies are using the unique properties of TiO_2 coatings to develop technologies and equipment for cleaning air and water [2].

Photocatalytic oxidation and heterogeneous photocatalysis permit solving important social and ecological problems [2]:

antibacterial action — sterilization, cleaning;

purifying air — removing harmful compounds in air, such as nitrogen and sulfur oxides and formaldehyde;

eliminating odors — decomposition of compounds which have an odor, such as acetaldehyde, ammonia, and hydrogen sulfide;

degassing — decomposition and elimination of organic compounds, such as cigarette smoke and oil residues which remain on surfaces;

purifying water — decomposition and removal of harmful compounds in sewage.

Photocatalysis is a process of oxidation or reduction of organic compounds or inorganic ions, which occurs with the participation of a photocatalyst under the action of light [3]. The formation of free charge carriers — electrons or holes — under irradiation of the surface of a photocatalyst (TiO_2) with light with wavelength < 390 nm plays the main role in splitting substances on the surface of a photocatalyst (Fig. 1).

Photocatalysts based on titanium oxide can also be used for producing antibacterial and self-cleaning coatings. Organic contaminants on glass coated with a TiO_2 film can be removed by exposure to sunlight. At the present time some foreign companies are producing on commercial scales self-cleaning glass and ceramic tiles with a TiO_2 coating: AFG Industries, Pilkington, PPG Industries, Deutsche Steinzeug Kerami, and AGC Flat Glass Europe [4]. Antibacterial coatings based on TiO_2 and $AgO – TiO_2$ films for glass microscope slides are well known. Photocatalytically active film

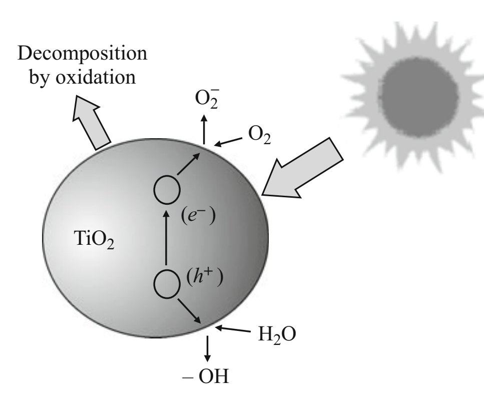

Fig. 1. Mechanism of photocatalytic action of TiO_2.

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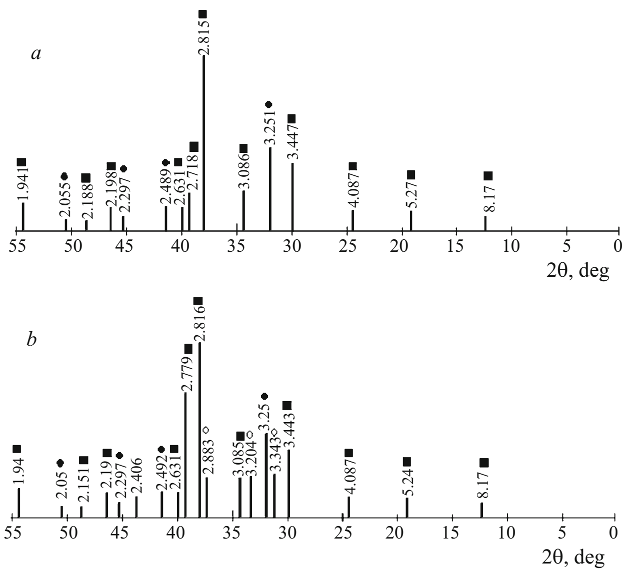

Fig. 2. Diffraction pattern of hydroxyapatite modified by titanium oxide: *a*) synthesized; *b*) heat-treated at 900°C; ■) $Ca_5(PO_4)_3OH$; ●) TiO_2 (rutile); ○) $Ca_3(PO_4)_2$.

coatings consisting of $AgO - TiO_2$ are characterized by bacteriacidal action against *Staphylococcus aureus* (NCTC 6571), *Escherichia coli* (NCTC 10418), and *Bacillus cereus* (CH70-2). This coating is recommended for use in hospitals, because it stability, reliability, cleanability, and strong antibacterial effect [5].

Various enameled steel products with new-generation antibacterial coatings are widely advertised. This includes electric water heaters, refrigerators, laundry and dish washing machines, kitchenware, pipes manufactured by the companies BOSH, Eiserwerke Duker Gmbh (Germany), Dupont, AOS Holding Company (USA) [6], "Kirovskii zavod" JSC (Russia) [7] and others. The antibacterial effect of enameled coatings is primarily due to the introduction of Ag^+ ions; silver, possessing a high affinity to sulfur blocks active centers of biochemical structure and binds – SH groups. However, the use of silver as a bactericidal additive greatly increases the cost of enamel products.

The importance of creating antibacterial glass enamel coatings is due to the desire to increase the standard of living as well as the need to lower the cost of well-known methods of obtaining bactericidal materials.

The objective of the present work is to synthesize inorganic powder based on hydroxyapatite modified by titanium oxide as a bactericidal additive in antibacterial glass enamel coatings. The well-known fact that materials can be made anticorrosive with respect to bioagents (fungi, bacteria) by adding titanium oxide in various matrices was taken into account.

To perform this work hydroxyapatite was precipitated from water solutions of the indicated components at pH > 6 followed by drying at 250°C. It was used as a matrix into which an filler was added — titanium oxide in the modification rutile with ratio $Ti^{4+}/(T^{4+} + Ca^{2+})$ equal to 0.03 – 0.07.

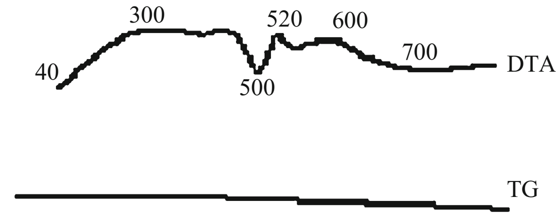

Fig. 3. Thermogram of synthesized hydroxyapatite modified by titanium oxide (number of the curve) temperature, °C).

The composition of the matrix — filler was mixed and passed through No. 63 sieve several times to obtain a uniform distribution of the filler in the matrix. The mixture was pressed in the form of cylinders with height and diameter equal to 1 cm. The modified hydroxyapatite was sintered at 580 – 660°C in a muffle furnace for 2 h.

X-ray phase analysis showed that the synthesized inorganic powder has hydroxyapatite structure with TiO_2 crystal inclusions (Fig. 2*a*).

According to the data presented in [9], HAP dehydration and decomposition processes largely depend on its stoichiometry, the atmosphere, and the water vapor partial pressure. When heated in air, starting at temperature 700°C, HAP with ration Ca/P < 1.67 partially decomposes into tricalcium phosphate (TCP).

XPA shows that identical qualitative changes of the phase composition of the inorganic powder in respect to HAP are also observed in the composition studied after heat treatment (Fig. 2*b*). The content of rutile is characterized by a constant content before and after heat-treatment, since it is a stable form of TiO_2 which is not prone to polymorphous transformations.

The decomposition of synthesized powder into HAP and TCP is recorded on the DTA curve at 700°C (Fig. 3), which agrees with the data presented in [9]. For synthesized powder an endothermal effect is observed at temperatures 480 – 500°C; this effect is characterized by a densification process, since in this region the linear dimensions change in connection with the removal of pores. According to the data of [10] this process on the dilatometric curve of HAP occurs above 600°C. The decrease of the temperature of densification of the HAP that we synthesized by 100°C is probably due to the method used to obtain HAP. The densification of the powder by occurs more rapidly in finely dispersed HAP powder obtained by the solution method, and this is seen in the displacement of the temperature of the process toward lower temperatures.

To determine the effectiveness of using synthesized powder as a bactericidal and fungicidal filler it was introduced into ÉSP-117 titanium glass enamel frit in amounts ranging from 1 to 5%[3] per 100% of frit and determined the anticorrosion effect.

[3] Here and below — content by weight.

TABLE 1. Antibacterial Properties of Synthesized Glass Enamel Coatings Based on ÉSP-117 Frit

Indicator	Antibacterial and antifungal properties of glass enamel coating with inorganic filled														
	NP-1			NP-2			NP-3			NP-4			NP-5		
$Ti^{4+}/(Ti^{4+} + Ca^{2+})$	0.03			0.04			0.05			0.06			0.07		
Mass content of inorganic filler, %	1	3	5	1	3	5	1	3	5	1	3	5	1	3	5
E_{ab}, %	55	60	60	60	60	75	65	65	80	85	85	85	90	90	90
E_{af}, %	45	45	50	60	60	70	65	65	75	75	75	80	82	85	85

Enameled plates were sterilized in an autoclave (at 200°C in 2 h). *Escherichia coli* and *Aspergillus niger* colonies were grown in broth at 37°C. Dissolved bacteria and fungi together with the solution were placed at the bottom Petri dishes in such a way that their layer was found in close contact with the enameled plate. The antibacterial activity of an enameled surface is determined as the degree to which the growth of bacteria and fungi on it is curtailed.

It was established that all synthesized composite glass enamel coatings based on ÉSP-117 frit and inorganic fillers, differing by the ratio $Ti^{4+}/(Ti^{4+} + Ca^{2+})$, are characterized by an antibacterial effect (E_{ab}) with respect to *Escherichia coli* and antifungal effect (E_{af}) with respect to *Aspergillus niger* (see Table 1). An increase of E_{ab} and E_{af} is used to characterize the compositions of the composite glass enamel coatings NP-4 and -5 with the content of the synthesized inorganic powder ranging from 1 to 5% with ratio $Ti^{4+}/(Ti^{4+} + Ca^{2+})$ = 0.06 – 0.07 and composite glass enamel coatings NP-2 and -3 with content of synthesized inorganic 5% with ration $Ti^{4+}/(Ti^{4+} + Ca^{2+})$ equal to 0.04 and 0.05, respectively. A decrease of E_{ab} and E_{af} is observed when the ratio $Ti^{4+}/(Ti^{4+} + Ca^{2+})$ decreases to 0.03 – 0.05 in the composite glass enamel coating NP-1 with content of the synthesized inorganic powder from 1 to 5%, and for NP-2 and -3 with content of the synthesized inorganic powder from 1 to 3%.

So, an analysis of the scientific – technical and patent literature established that heterogeneous photocatalysis is promising for obtaining the antibacterial and antifungal effects of glass enamel coatings. A bactericidal powder based on hydroxyapatite, modified by titanium oxide, was synthesized and its phase composition was investigated. It was established that the composite glass enamel coatings are characterized by substantial antibacterial and antifungal effects. The highest values of the indicators E_{ab} from 75 to 90% and E_{af} from 70 to 85% are observed in glass enamel coatings with HP-4 and -5 fillers whose content ranges from 1 to 5% and ratio $Ti^{4+}/(Ti^{4+} + Ca^{2+})$ equal to 0.06 – 0.07 and in coatings with fillers HN-2 and -3 with content 5% and ratio $Ti^{4+}/(Ti^{4+} + Ca^{2+})$ equal to 0.4 and 0.5, respectively.

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